Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 43 (2012) 312 – 317

Procedia Engineering

www.elsevier.com/locate/procedia

International Symposium on Safety Science and Engineering in China, 2012 (ISSSE-2012)

Thermal Decomposition Analysis and Safety Study on Di-tert-butyl Peroxide

Lv Jiayu[a], Chen Wanghua[a,*], Chen Liping[a], Tian Yingtao[a], Sun Xin[a]

[a]*Dept. of Safety Eng., Nanjing University of Science and Technology, Jiangsu, 210094, China*

Abstract

Di-tert-butyl peroxide (DTBP) is widely used as modifier, cross-linking agent and polymerization initiator in industry although it is a reactive and exothermically unstable peroxide. So far, available thermal analyses were most based on DTBP in diluents. Thermal activities of pure DTBP (97% purity) were studied in this paper, and as a contrast, 20% mass concentration DTBP in toluene was also investigated. Thermal analysis apparatus, thermal screening unit (TSu) and accelerating rate calorimeter (ARC), were employed to supply basic thermodynamic and kinetic parameters such as detectable exothermic onset temperature T_0, heat of decomposition Q, maximum temperature rise rate $(dT \cdot dt^{-1})_{max}$, maximum pressure rise rate $(dP \cdot dt^{-1})_{max}$, activation energy E, and frequency factor A, etc. On the basis of thermal study, it was demonstrated that toluene was not a good diluent for DTBP and pure DTBP was more danger compared to DTBP in diluents.

Keywords: Di-tert-butyl peroxide (DTBP), Thermodynamic, Kinetic, Thermal screening unit (TSu), Accelerating rate calorimeter (ARC)

1. Introduction

With fast development of industry and wide usage of organic peroxides, the hazard assessment of organic peroxides become more and more important in many countries [1-5]. As a kind of common organic peroxides, di-tert-butyl peroxide (DTBP, $C_8H_{18}O_2$) has been employed as modifying agent to promote aridity in lots of oils and glossiness in plastic production field. And it also has been used as cross-linking agent in rubber production and polymerization initiator in production processes of polystyrene and polypropylene [6-7]. Although DTBP is regarded as one of a relatively stable organic peroxides, great damages would be brought to the production process, workers and environment once the runaway reaction happens.

Thermal analyses have been carried out by different thermal analysis apparatuses on organic peroxides. Chun-Ping Lin [8] studied the thermokinetic parameters of tert-butyl peroxybenzoate (TBPB) by thermal activity monitor (TAM ш) and differential scanning calorimeter (DSC), and a green thermal analysis was developed for a reactor containing TBPB to prevent pollution and reduce the energy consumption. Xin-Rui Li [9] investigated the thermal decomposition of several liquid organic peroxides, such as t-Butyl peroxy acetate (TBPA), DTBP and cumene hydroperoxide (CHP), and determined the thermal runaway and reactive hazards potential of organic peroxides.

* Corresponding author. Tel.:+86-025-84315526-8005.
E-mail address: chenwh_nust@163.com

1877-7058 © 2012 Published by Elsevier Ltd. Open access under CC BY-NC-ND license.
doi:10.1016/j.proeng.2012.08.054

In this paper, thermodynamic and kinetic parameters of DTBP such as detectable exothermic onset temperature T_0, heat of decomposition Q, maximum temperature rise rate $(dT \cdot dt^{-1})_{max}$, maximum pressure rise rate $(dP \cdot dt^{-1})_{max}$, activation energy E, and frequency factor A were obtained by thermal screening unit (TSu) and accelerating rate calorimeter (ARC). Based on these thermal data, safety studies were done on pure DTBP and DTBP in toluene to distinguish dangers caused by the two hazardous material systems.

2. Experimental

Thermal and dynamic properties of DTBP (97% purity) and 20 mass% DTBP in toluene were studied by two different instruments.

2.1. Fundamental thermal screening by TSu

Except for temperature testing, TSu, manufactured by Hazard Evaluation Laboratory in Britain, is a thermal screening unit equipped with a pressure transducer to obtain the pressure history of samples as reaction proceeds. During the process of tests, users can set up the ramp rates of the oven. After an initial delay due to "thermal lagging" effects, the sample temperature will be found to follow the oven ramp at the same rate with a slight offset.

5 g of the 20% DTBP mixture and 1g sample of pure DTBP were charged into 316ss test cells, 8mL in volume, and the temperature were both ramped in 2°C·min^{-1} from 25 to 300°C.

2.2. Adiabatic tests by ARC

Experiments were carried out in esARC, produced by Thermal Hazard Technology Company in Britain. Here, the measurement temperature range is from 30 to 500 ºC, pressure can be logged is from 1 to 150 bar and the sensitivity is 0.02°C·min^{-1}. By gaining basic information of T_0, T_{end} and Q from tests, E and A could be calculated.

3. Results and discussions

3.1. Thermal decomposition analysis by TSu

The thermal screening results of 20 % DTBP solution and pure DTBP at 2 ºC ·min^{-1} are presented in Fig. 1 to Fig. 2.

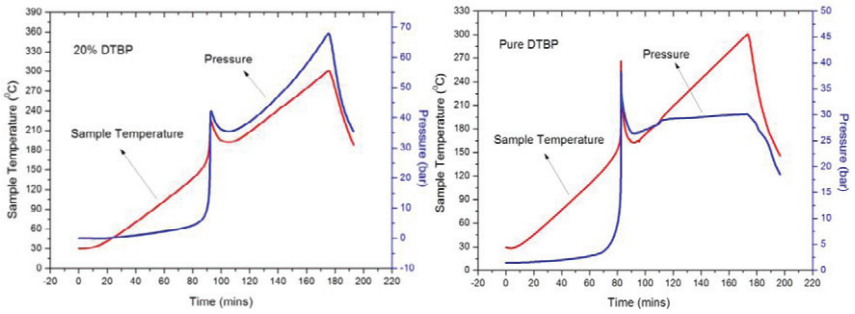

Fig. 1. Temperature and pressure histories of DTBP at ramping rate of 2°C·min^{-1}

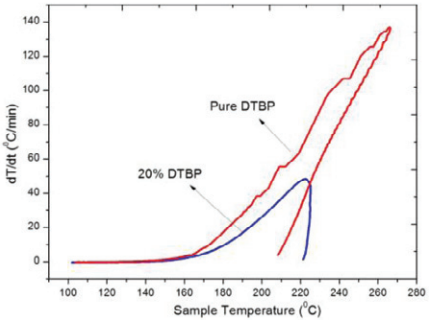

Fig. 2. Temperature rates vs. temperature of DTBP by TSu

Fig.1 shows the exothermic peak shapes of two samples have a slight difference that the pure one is sharper and narrower. T_0 of both samples were detected as 150 ºC around according to Fig.2. The measured maximum temperatures and pressures of 20% DTBP and pure one are 225 ºC, 43 bar and 270 ºC, 38 bar respectively. 45 ºC maximum temperature increase of pure DTBP indicates a higher severity once thermal decomposition was triggered. However, the maximum pressure of pure DTBP is 5 bar lower which obscure the determination of thermal hazard for the two samples. It is known that the boiling point of toluene is 110 ºC, lower than T_0 of 20% DTBP, and the evaporation of this solvent will certainly bring high pressure to the whole system. To eliminate the influence caused by vapor pressure of solvent, another test of 4 g toluene was carried out which was showed in Fig.3. By polynomial fit technique, the accurate equation of pressure and temperature can be obtained below.

y=2.572×10-6x3-5.307×10-4x2+0.048x+0.385

where x refers to temperature (ºC) and y stands for pressure (bar).

By subtracting the vapor pressure of toluene based on equation fitted above, the pressure contributed by DTBP in the mixed system was obtained and presented in Fig.4, which showed that the three different pressure curves were in good accordance with each other in trends. And it was showed that pressure caused by pure DTBP's decomposition was 10 bar higher than 20% DTBP subtracting toluene, which reached a consensus on severity determined by T_f. That is to say pressure contributed by 1g DTBP in toluene was less than 1g DTBP in pure sample system. Therefore, stable diluents can reduce the hazards caused by DTBP if runaway reactions happen. However, the low boiling point of toluene excludes it from the ranks of applicable diluents. Consequently, people cannot predict temperature and pressure histories of pure DTBP according to those of DTBP in solutions although it is useful in avoiding blasting of test cells.

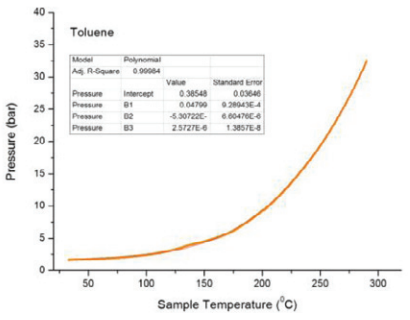

Fig.3. Pressure vs. temperature of toluene by TSu

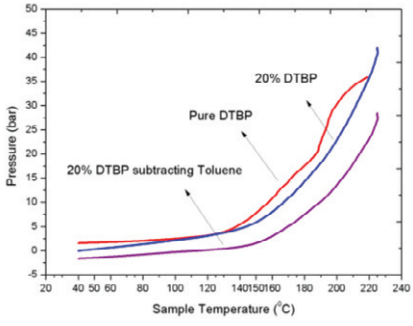

Fig.4. Pressure vs. temperature of DTBP in different situations by TSu

3.2. Thermal decomposition analysis by ARC

3.2.1. Calculation basis

Experiments were run under adiabatic processes in HWS mode, so the reaction rate follows Arrhenius rate equation:

$$\frac{dc}{dt} = -Ac^n \exp(-\frac{E}{RT}) \tag{1}$$

Where c is the concentration of reactants, t is time, n is the reaction order, R is the gas constant and T is absolute temperature.

For an adiabatic system, heat generated during reaction is entirely used to raise the temperature of the whole system, so adiabatic equation below can be obtained:

$$Q\frac{dc}{dt} = -C_{\mathrm{p}}\frac{dT}{dt} \tag{2}$$

Where Q is the heat of reaction and C_p is the average specific heat capacity.

Combined equations (1) with (2), equation (3) below can be obtained:

$$\frac{dT}{dt} = \frac{Q}{C_p}Ac^n \exp(-\frac{E}{RT}) \tag{3}$$

Under certain boundary conditions,

When t=0, then c=c_0, T=T_0,

And when t=∞, then c=0, T=T_f. (4)

Calculate equation (2) using the boundary conditions, equation (5) can be present as follow:

$$\frac{Q}{C_p} = \frac{T_f - T}{c_0} = \frac{\Delta T}{c_0} \tag{5}$$

Where c_0 is initial concentration of the reactant.

3.2.2. Results of thermal analysis

Based on equations (1) to (5) and the experimental data, thermokinetic parameters calculated were shown in Table 1 and the main curves obtained by esARC were presented in Fig.5 and Fig.6.

Table 1. Thermokinetic parameters of DTBP and 20% DTBP

Samples	Q ($J{\cdot}g^{-1}$)	n	E ($kJ{\cdot}mol^{-1}$)	A (s^{-1})
DTBP	463.64	1	170.61	1.06×10^{20}
20% DTBP	251.77	1	164.32	4.33×10^{18}

Table 1 indicated that, reflecting by Q, DTBP in solution are more stable than pure DTBP. Nearly twice Q value of pure DTBP than 20% DTBP means that the former has more hazards in its production and transportation processes. It is known that higher activation energy gives higher temperature sensitivity. The approximate E values of both samples indicate a equivalent sensitivity of decomposition reactions. Once decomposition happens, the system which contains pure DTBP will have higher reaction rates according to A.

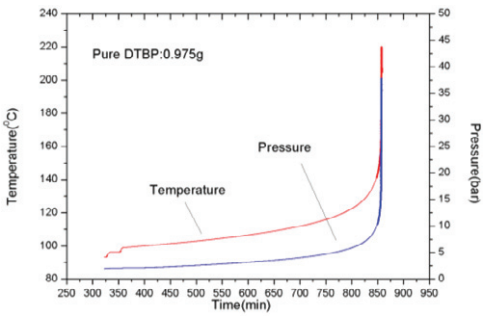

Fig.5. Temperature and pressure histories of pure DTBP

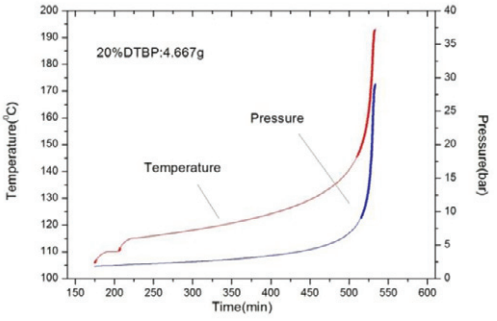

Fig.6. Temperature and pressure histories of 20% DTBP

It can be seen in Fig.5 and Fig.6 that after a time period called time to maximum reaction rates θ, pressure and temperature in the whole systems had rapid rises. For pure DTBP, θ is about 850min and for 20% DTBP, it is about 525min. This phenomenon illustrates that the vaporization of toluene shortened the time for rescuing if runaway reaction happens, and at the same time emphasizes that toluene is not suitable for DTBP's dilute during storage and transportation.

T_0 of 20% DTBP, 15 ºC higher than pure one, is 115 ºC, with T_f and P_f values of 193 ºC and 29 bar respectively. Detected T_f and P_f of pure DTBP were presented as 220 ºC and 38 bar. Lower T_0 value of pure DTBP indicates a higher possibility for trigging decomposition reaction. Differ from the TSu result that P_f of pure DTBP obtained by ARC was higher than 20% DTBP system, and that is because T_f of 20% DTBP system was 193ºC, 32 ºC lower than that tested by TSu, which brought less vapor pressure of toluene. Therefore, although 20% DTBP is more stable than pure DTBP, toluene is still an inadequate diluent for DTBP.

For further analyzing of samples' thermal stabilities, histories of another two parameters, $dT \cdot dt^{-1}$ and $dP \cdot dt^{-1}$, were shown in Fig.7 and Fig.8.

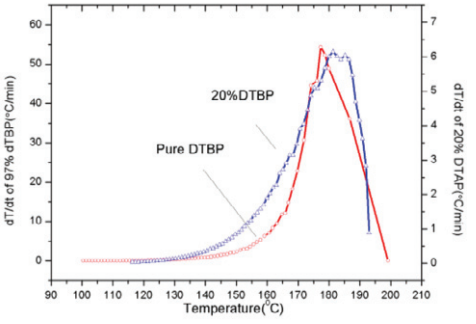

Fig.7. Temperature rate of two different samples

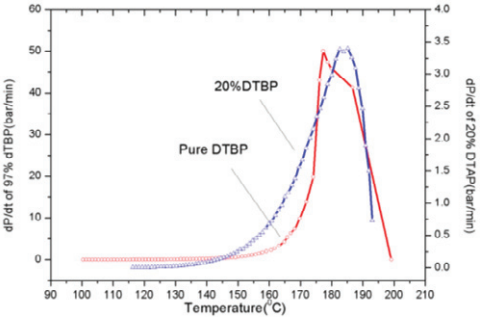

Fig.8. Pressure rate of two different samples

In Fig.7 and Fig.8, it was obvious that the values of $(dT \cdot dt^{-1})_{max}$ and $(dP \cdot dt^{-1})_{max}$ were reached at nearly the same temperature, around 180 ºC, but the values of temperature rate or pressure rate between pure DTBP and 20% DTBP were of great differences. $(dT \cdot dt^{-1})_{max}$ and $(dP \cdot dt^{-1})_{max}$ for pure DTBP are approximately 9 times and 16 times greater than that of 20 % DTBP respectively, which showed the pure DTBP was much more dangerous. Although DTBP was considered as one of the most stable organic peroxides, safety precaution (such as stored in diluents) should be taken to keep it much safer in production and transportation processes.

4. Conclusions

As a kind of common organic peroxides, DTBP was in unsteady state when exposed to outer heating sources and may be dangerous in the production and transportation processes. Thermal tests were run with TSu and ARC and the heat of decomposition was calculated under adiabatic conditions, which indicated that pure DTBP had a high severity due to its great quantity of heat during decomposition. Theoretical analysis showed that a first order reaction was the main way of thermal decomposition and E value of 20% DTBP and pure DTBP were 164 and 170kJ·mol^{-1} respectively. Comparing pure DTBP with DTBP solution under linear temperature program and heat-wait-search model, results showed that pure DTBP was more dangerous than DTBP solution. Due to the lower boiling point of toluene compared to T_0 of the tested system,

DTBP in toluene can not reflect the real pressure situations of pure DTBP. And toluene is not suggested to be diluent for DTBP in manufacture, storage and transport.

References

[1] Jen-Hao Chi, Sheng-Hung Wu, Chi-Min Shu, 2009. Thermal Explosion Analysis of Methyl Ethyl Ketone Peroxide by Non-isothermal and Isothermal Calorimetric Applications, Journal of Hazardous Materials 171, p. 1145.
[2] Markert H, Wiedenmann R., 1973. Crosslinking of Polyethylene in the Presence of Addititives Part 1, Siemens Forsch 2, p. 85.
[3] Yu.A Alexandrov, S.A. Lebedev, R.V. Kuznetsova, 1980. Thermal Decomposition of Organo-zinc and Cadmium Peroxides in Hydrocarbons, Journal of Organometalic Chemistry 201, p. 21.
[4] K.W. Wu, H.Y. Hou, C.M. Shu, 2006. Thermal Phenomena Studies for Dicumyl Peroxide at Various Concentrations by DSC, Journal of Thermal Analysis and Calorimetry 83, p. 41.
[5] Jasbir Singh, Cormac Simms, 1999. The Thermal Screening unit (TSu) a Tool for Reactive Chemical Screening, Journal of Thermal Analysis and Calorimetry 58, p.193.
[6] Zhi-Min Fu, Xin-Rui Li, Hiroshi Koseki, Yun-SooMok, 2003. Evaluation on Thermal Hazard of Methyl Ethyl Ketone Peroxide by Using Adiabatic Method, Journal of Loss Prevention in Process Industries 16, p. 389.
[7] Po-Yin Yeh, Chi-Min Shu, Yih-Shing Duh, 2003. Thermal Hazard Analysis of Methyl Ethyl Ketone Peroxide, Industries in Engineering Chemical Research 42, p.1.
[8] Chun-Ping Lin, Jo-Ming Tseng, Yi-Ming Chang, 2012. Green Thermal Analysis for Predicting Thermal Hazard of Storage and Transportation Safety forTert-butyl Peroxybenzoate, Journal of Loss Prevention in Process Industries 25, p.1.
[9] Xin-Rui Li, Hiroshi Koseki, 2005. Thermal Decomposition Kinetic of Liquid Organic Peroxides. Journal of Loss Prevention in Process Industries 18, p. 460.